

Seeking for reliable double-hybrid density functionals without fitting parameters: The PBE0-2 functional

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Without the use of any empirical fitting to experimental or high-level *ab initio* data, we present a double-hybrid density functional approximation for the exchange-correlation energy, combining the exact Hartree-Fock exchange and second-order Møller-Plesset (MP2) correlation with the Perdew-Burke-Ernzerhof (PBE) functional. This functional, denoted as PBE0-2, is shown to be accurate for a wide range of applications, when compared with other functionals and the *ab initio* MP2 method. The qualitative failures of conventional density functional approximations, such as self-interaction error and noncovalent interaction error, are significantly reduced by PBE0-2.

I. INTRODUCTION

Over the past two decades, Kohn-Sham density functional theory (KS-DFT) [1] has become a very popular electronic structure method for molecular and solid-state systems, due to its computational efficiency and reasonable accuracy. Although the exact exchange-correlation (XC) density functional $E_{xc}[\rho]$ in KS-DFT remains unknown, accurate approximations to $E_{xc}[\rho]$ have been continuously developed to extend the applicability of KS-DFT to a wide range of systems [2].

The hierarchy of approximations to $E_{xc}[\rho]$ has been formulated as a *Jacob's ladder* connecting the earth (Hartree theory) to the heaven (chemical accuracy) [3]. The first rung of the ladder is the local density approximation (LDA) [4, 5], representing the XC energy density by the local density. Going beyond the LDA, there has been an increasing interest in the “parameter-free” functionals developed by Perdew and co-workers, such as PBE [6] and TPSS [7], demonstrating the usefulness of these functionals. As LDA, PBE, and TPSS belong to the first, second, and third rungs of the ladder, respectively, they systematically improve upon the description of short-range XC effects by climbing up the ladder (with slightly increasing computational costs). However, due to the lack of accurate treatment of nonlocal XC effects, these semilocal functionals (first three rungs) can lead to significant errors, characterized by self-interaction error (SIE), noncovalent interaction error (NCIE), and static correlation error (SCE), in situations where these failures occur [2, 8].

The SIEs of density functional approximations (DFAs) can be reduced by hybrid DFT methods (fourth rung) [9], combining a fraction of the exact Hartree-Fock (HF) exchange with a semilocal functional. As the fraction of HF exchange included in a hybrid functional can be rationalized by perturbation theory arguments [10], the

PBE-based hybrid functional PBE0 [11], has gradually gained its popularity. In view of the successive evolution of the PBE-based functionals: LDA (first rung) \rightarrow PBE (second rung) \rightarrow TPSS (third rung) \rightarrow PBE0 (fourth rung) \rightarrow ? (fifth rung), naturally, the question is, what could be a functional on the fifth rung (highest rung) of the ladder? In this work, we propose a PBE-based double-hybrid functional (fifth rung), and demonstrate its superiority to the functionals on the first four rungs of the ladder, for a wide range of applications.

II. THE PBE0-2 FUNCTIONAL

The SIEs and NCIEs associated with DFAs can be simultaneously reduced by double-hybrid methods (fifth rung) [12–17], combining a fraction of HF exchange and a fraction of second-order Møller-Plesset (MP2) correlation [18] with a semilocal functional. Accordingly, a PBE-based double-hybrid functional is given by

$$E_{xc} = a_x E_x^{\text{HF}} + (1 - a_x) E_x^{\text{PBE}} + (1 - a_c) E_c^{\text{PBE}} + a_c E_c^{\text{MP2}}, \quad (1)$$

where E_x^{HF} is the HF exchange, E_x^{PBE} is the PBE exchange, E_c^{PBE} is the PBE correlation, and E_c^{MP2} is the MP2 correlation (a perturbative term evaluated with the orbitals obtained using the first three terms of the energy). In this work, the two mixing parameters, a_x and a_c , are determined by physical arguments (i.e., without the use of any empirical fitting to experimental or high-level *ab initio* data).

Based on the double-hybrid approximations proposed by Sharkas, Toulouse, and Savin [19], and the closely related work of Brémont and Adamo [20], Toulouse *et al.* [21] have proposed the linearly scaled one-parameter double-hybrid (LS1DH) approximation (see Eq. (10) of Ref. [21]), showing the relationship between the mixing parameters, a_x and a_c , in a double-hybrid functional,

$$a_c = (a_x)^3. \quad (2)$$

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Applying Eq. (2) to Eq. (1), only one of the mixing parameters needs to be determined.

Functionals on the first four rungs of the ladder fail to describe long-range van der Waals (vdW) interactions in regions where there is no overlap of the subsystems, due to the lack of long-range correlation effects [2, 22]. This problem can be greatly reduced by the DFT-D (KS-DFT with empirical dispersion corrections) schemes [17, 23–25] or by a fully nonlocal density functional for vdW interactions (vdW-DF) [26], showing generally acceptable performance on several noncovalent systems [27].

By contrast, the MP2 correlation in a double-hybrid functional is itself fully nonlocal, and thus responsible for describing long-range vdW interactions. To determine the fraction a_c of MP2 correlation in Eq. (1), consider the two limiting cases where $a_c = (a_x)^3 = 0$ and $a_c = (a_x)^3 = 1$, which reduce to PBE and MP2, respectively. In view of the underbinding tendency of PBE and overbinding tendency of MP2 in describing the interaction energies of many vdW complexes, a mixing of 50% of PBE correlation with 50% of MP2 correlation seems physically justified (as vdW interactions are inherently *correlation* effects). Employing this half-and-half mixing of the PBE and MP2 correlation functionals with the LS1DH approximation in Eq. (2), we obtain

$$a_c = 1/2, \quad a_x = (1/2)^{1/3} \approx 0.793701. \quad (3)$$

Our resulting PBE-based double-hybrid functional, defined in Eqs. (1) and (3), is denoted as PBE0-2, where the “0” refers to no fitting parameters, and the “-2” refers to the post-KS treatment for the MP2 correlation.

By contrast, the mixing parameters $a_x = 1/2$ and $a_c = (1/2)^3 = 1/8$, are adopted in PBE0-DH [20], another PBE-based double-hybrid functional (also based on Eqs. (1) and (2)), wherein a half-and-half mixing of the PBE and HF exchange functionals is *effectively* employed. Therefore, a comparison between the performance of PBE0-2 and PBE0-DH is particularly important, as it shows the significance of the physical arguments used in determining the a_x and a_c .

III. RESULTS

For a comprehensive comparison of different functionals, we examine the performance of PBE0-2, other PBE-based functionals (LDA [4, 5], PBE [6], TPSS [7], PBE0 [11], and PBE0-DH [20]), three popular functionals (B3LYP (a hybrid functional) [9, 28], B2PLYP (a double-hybrid functional) [14], and B2PLYP-D3 (a double-hybrid functional with empirical dispersion corrections) [17]), and the *ab initio* MP2 method [18], on various test sets involving the 223 atomization energies (AEs) of the G3/99 set [29–31], the 40 ionization potentials (IPs), 25 electron affinities (EAs), and 8 proton affinities (PAs) of the G2-1 set [32], the 76 barrier heights of the NHTBH38/04 and HTBH38/04 sets [33, 34], the 22 noncovalent interactions of the S22 set [35, 36], the 66

noncovalent interactions of the S66 set [37], two interaction energy curves of weakly bound complexes, isodesmic reaction energies, and two dissociation curves of symmetric radical cations, with a development version of Q-Chem 3.2 [38]. Detailed information about some of the test sets can be found in Ref. [39]. The error for each entry is defined as (error = theoretical value – reference value). Spin-restricted theory is used for singlet states and spin-unrestricted theory for others. Results are computed using the 6-311++G(3df,3pd) basis set, unless noted otherwise. For efficiency, the resolution-of-identity (RI) approximation [40] is used for calculations with the MP2 correlation (using sufficiently large auxiliary basis sets). The interaction energies of the weakly bound systems are computed with the counterpoise correction [41] for the basis set superposition errors (BSSE).

As shown in Table I, for the AEs of the G3/99 set, B2PLYP and B2PLYP-D3 have the best performance (partly due to the fact that this test set overlaps with their training sets). PBE0-2 performs similarly to PBE0-DH, PBE0, TPSS, and B3LYP, and significantly outperforms LDA, PBE, and MP2. For the IPs, EAs, and PAs of the G2-1 set, LDA performs poorly, while all the other functionals perform similarly to MP2. For the barrier heights of the NHTBH38/04 and HTBH38/04 sets, PBE0-2, PBE0-DH, B2PLYP, and B2PLYP-D3 have comparable performance, and are the best functionals here [42]. For the noncovalent interactions of the S22 and S66 sets, B2PLYP-D3 performs the best (mainly due to the empirical dispersion corrections). PBE0-2 performs similarly to MP2, and significantly outperforms all the other functionals [42].

Here, we calculate the interaction energy curves for the parallel-displaced (in Fig. 1) and T-shaped (in Fig. 2) configurations of the benzene dimer as functions of the intermonomer distance R (defined in Ref. [37]), where the optimized geometries and reference values are taken from the S66×8 set [37]. Overall, the predicted interaction energy curves of B2PLYP-D3 and PBE0-2 are the closest ones to the reference curves (within an error of 1 kcal/mol). LDA predicts too short equilibrium distances, and all the other functionals predict severely underbinding or even repulsive curves. MP2 incorrectly predicts the parallel-displaced configuration to be more stable than the T-shaped one.

The isodesmic reaction energies of n -alkanes to ethane have been known to give systematic errors in conventional DFT calculations [43–47]. The considered bond separation reaction,



was first proposed by Redfern *et al.* [43] to show the errors of B3LYP systematically increase as the number of chain units in n -alkanes, m , increases. To assess how PBE0-2 improves upon this problem, we calculate the isodesmic reaction energies of n -alkanes to ethane, where the optimized geometries and reference values are taken from Ref. [46]. As shown in Fig. 3, the predicted reac-

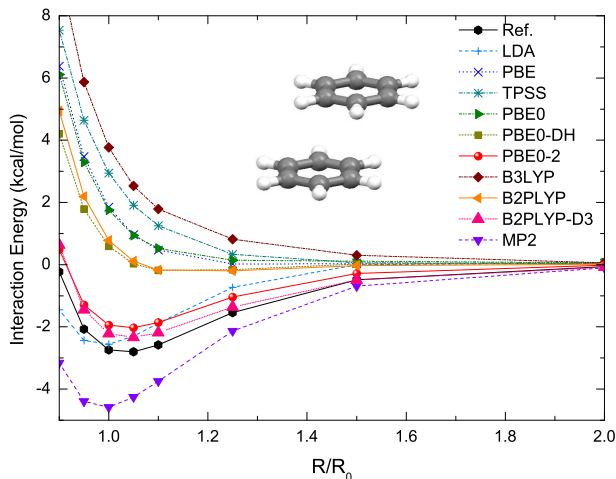


FIG. 1. Interaction energy curve for the parallel-displaced configuration of the benzene dimer as a function of the intermonomer distance R (defined in Ref. [37]), where R_0 is the equilibrium distance.

tion energies of PBE0-2 are extremely close to the reference values (within an error of 0.02 kcal/mol), due to its accurate treatment of medium-range correlation effects [46]. By contrast, all the other functionals and MP2 exhibit systematic errors with the increase of m . Note that B2PLYP-D3 overcorrects the systematic errors of B2PLYP.

Due to the severe SIEs of semilocal functionals, spurious fractional charge dissociation can occur, especially for symmetric charged radicals X_2^+ [48], such as He_2^+ and Ar_2^+ . To examine how PBE0-2 improves upon the SIE problem, spin-unrestricted calculations, using the aug-cc-pVQZ basis set, are performed. The DFT results are compared with results from MP2 theory and the highly accurate CCSD(T) theory [49]. As can be seen in Fig. 4, the predicted He_2^+ binding energy curve of PBE0-2 is very close to the CCSD(T) curve. It appears that the SIE associated with PBE0-2 is more than three times smaller than the next best DFT method shown. For Ar_2^+ , PBE0-2 can dissociate it correctly (see Fig. 5), which is a very promising result. However, a discontinuity undesirably appears in the derivative of PBE0-2 binding energy curve for Ar_2^+ , due to the use of MP2 correlation (as discussed in Refs. [16, 50]).

IV. CONCLUSIONS

In summary, we have developed a PBE-based double-hybrid functional, employing a half-and-half mixing of the PBE and MP2 correlation functionals with the LS1DH approximation in Eq. (2). Owing to its significant improvement over LDA, PBE, TPSS, and PBE0, this functional, denominated PBE0-2, fits well into the fifth rung of the ladder. Our results indicate that PBE0-2 is generally comparable or superior to PBE0-DH in per-

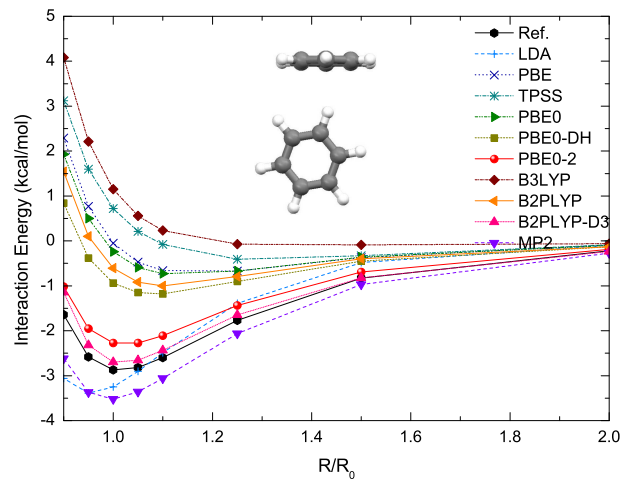


FIG. 2. Same as Fig. 1, but for the T-shaped configuration.

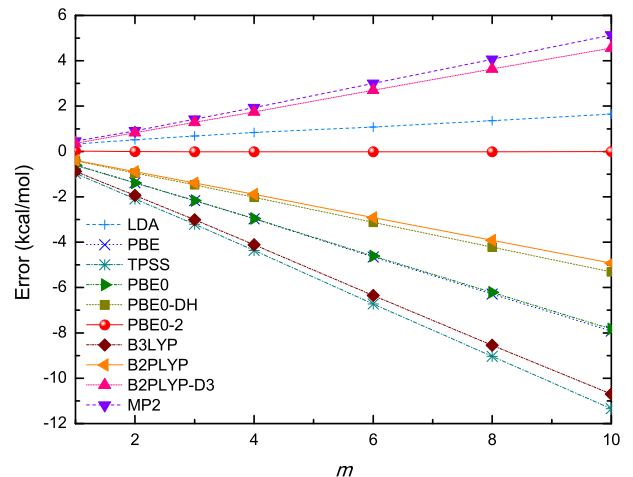


FIG. 3. Errors for isodesmic reaction energies of n -alkanes to ethane.

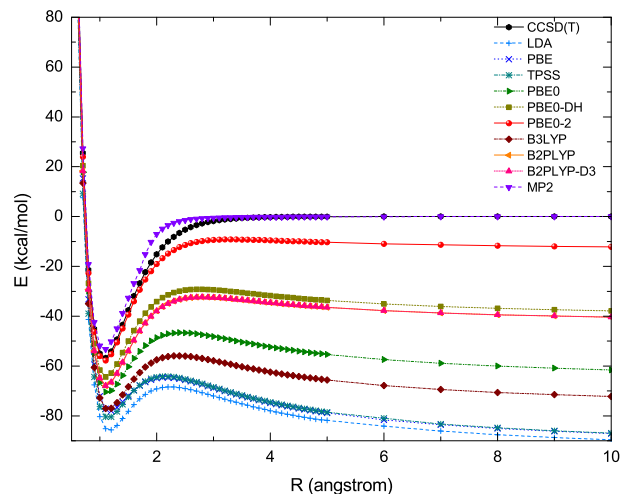
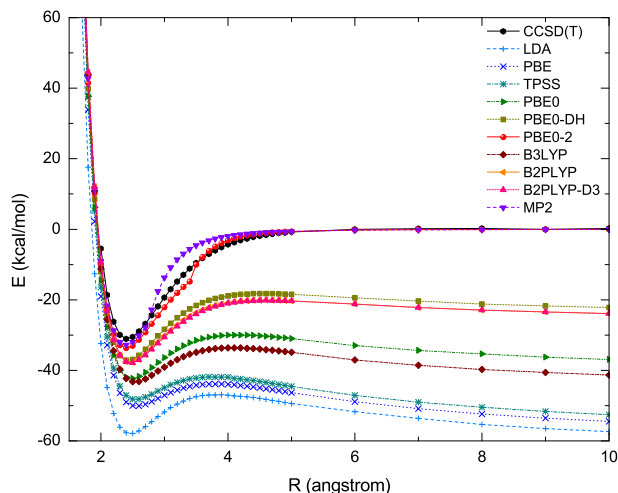


FIG. 4. Dissociation curve of He_2^+ . Zero level is set to $E(\text{He}) + E(\text{He}^+)$ for each method.

TABLE I. Mean absolute errors (in kcal/mol) of 10 methods for various test sets (see text for details).

System	PBE-based functionals						Other functionals			<i>Ab initio</i>
	LDA	PBE	TPSS	PBE0	PBE0-DH	PBE0-2	B3LYP	B2PLYP	B2PLYP-D3	MP2
G3/99 (223)	121.26	21.51	5.30	6.29	5.11	5.82	5.48	3.97	2.98	9.18
IP (40)	5.73	3.45	3.59	3.48	3.17	2.38	3.79	2.35	2.35	3.69
EA (25)	5.03	2.41	2.61	3.10	3.55	3.01	2.38	2.16	2.17	3.95
PA (8)	5.91	1.60	1.81	1.14	1.09	0.96	1.16	1.18	1.13	0.96
NHTBH (38)	12.62	8.62	9.16	3.63	1.57	2.44	4.69	2.19	2.44	5.48
HTBH (38)	17.95	9.67	8.68	4.60	2.01	1.39	4.56	2.17	2.45	3.38
S22 (22)	2.03	2.72	3.56	2.46	1.78	0.61	3.90	2.25	0.22	0.89
S66 (66)	1.85	2.23	3.09	2.10	1.58	0.67	3.33	1.96	0.21	0.45

FIG. 5. Same as Fig. 4, but for Ar_2^+ .

formance. As PBE0-2 contains a very large fraction ($\approx 79\%$) of HF exchange and a large fraction (50 %) of MP2 correlation, the SIE and NCIE associated with PBE0-2 are significantly reduced, reflecting its superior performance for self-interaction problems and noncovalent interactions, respectively. However, due to the perturbative treatment of nonlocal correlation, the SCE of PBE0-2 can be enormous in situations where strong static correlation effects are pronounced [2, 8]. It remains challenging to develop a generally accurate density functional resolving all the qualitative failures of semilocal approximations at a reasonable computational cost.

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